ALTERATION OF CIGARETTE SMOKE COMPOSITION I. INFLUENCE OF CERTAIN ADDITIVES[1]

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The influence of tobacco additives on the composition of the combustion products in the mainstream smoke gas from modified cigarettes is discussed. Substances which are alleged to cause harmful effects to the ciliated passages, such as carbon monoxide, hydrogen cyanide, and acrolein, were determined by colorimetric or gas chromatographic techniques. Other components, for which quantitative data are presented, include hydrogen sulfide, sulfur dioxide, formaldehyde, nitrogen oxides, hydrogen, carbon dioxide, oxygen, methanol, acetonitrile, acetaldehyde, acetone, and some hydrocarbons. Many of the additives produced measurable changes in the coal-burning temperatures ($-50°C$ to $+28°C$), as well as significant changes in the composition of the mainstream smoke gases. Most noticeable effects were observed with the addition of sodium nitrate and nickel oxalate to the tobacco. In general, those additives which supplied oxygen to the combustion process were found to significantly alter the combustion process.

INTRODUCTION

Attempts to modify the chemical composition of cigarette smoke by eliminating deleterious substances not necessary to pleasing aroma and flavor have been continuing for some time (1-3). Among the approaches taken, smoke filtration has been the most popular, and perhaps the most convenient. However, other methods for altering cigarette smoke have been reported, including the use of additives, for example, that lower (or raise) the combustion temperature of cigarettes, or in some other way influence combustion processes (4). Generally, effectiveness of these approaches (filters, additives) has been determined by measuring changes either in the concentration of selected particulate phase components (5) or in burn temperature (4).

During the study described herein, ways were sought to effect favorable concentration changes in the vapor phase (as opposed to the particulate phase) of cigarette smoke, since many of the constituents of the vapor phase (e.g. nitrogen oxides, acrolein, acetonitrile, formaldehyde, hydrogen cyanide, carbon monoxide, *inter alia*) are believed to contribute to the alleged detrimental consequences of cigarette smoking (1-3, 6). Initially, our efforts were based on the use of selected cigarette additives; subsequently, we were able to effect marked changes in the level of components in the vapor phase by modifying the physical design of the cigarette. The present paper describes the first of these two approaches and details the results obtained.

EXPERIMENTAL

Additives: Additives screened in the present study include:

1) Sodium nitrate
2) Basic Magnesium Carbonate
3) Petroleum reforming catalyst (Houdry Process and Chemical Co.)
4) Lead borate glass
5) Nickel oxalate
6) Benzothiazyl disulfide
7) "HZ-1" Catalyst (Houdry Process and Chemical Co.)
8) "Vazo" (Azo-bis-isobutyronitrile)

Preparation of cigarettes: Additives, after being reduced to a powder of 200 mesh, were mixed with humidified tobacco (taken from commercial cigarettes) in a sealed plastic bag. From the resulting mixture, cigarettes (85 mm long) were fabricated on a Deluxe V-Master Cigarette Machine[2] (4). Additive concentrations in treated cigarettes ranged from 8 to 10%. Reference cigarettes were fabricated in the same way from the same tobacco, but without additive. The commercial cigarettes (85 mm long), from which the tobacco was taken to fabricate the reference and test cigarettes, served as conrols.

Smoking apparatus: A smoking apparatus (**Figure 1**) similar to that described by Newsome et al. (7) was constructed for the purpose of delivering a 35 ml puff of filtered smoke, of 2-second duration, into an appropriate smoke collection flask (**Figure 1**).

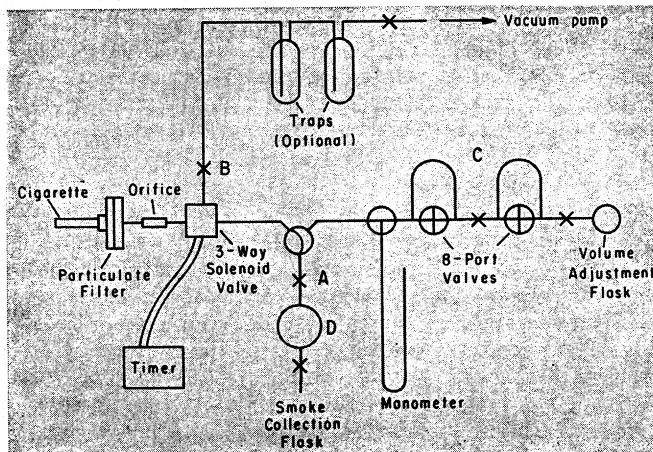*Sampling procedure:* All analytical data were obtained on the fifth puff of the cigarette. The puffing sequence

Fig. 1—Schematic of smoking apparatus.
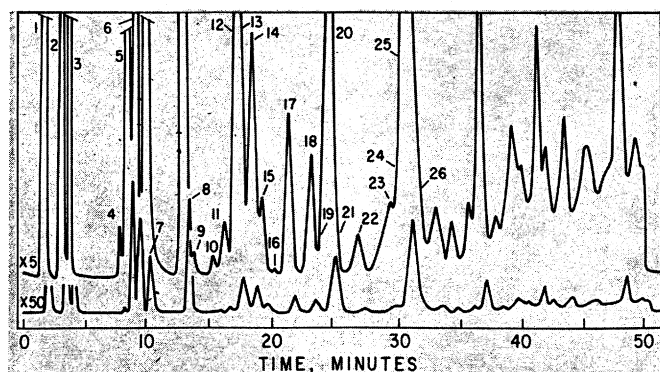
Fig. 2—Gas chromatogram of vapor phase of cigarette smoke (from control cigarette).

1. Methane
2. Ethene
3. Ethane
4. Propadiene
5. Propene
6. Propane
7. {Propyne / Methyl Chloride
   {Methanol
8. Acetaldehyde
9. Ethylene Oxide
10. Unidentified
11. Methyl Formate
12. {Butene-1 / Butadiene
13. Ethanol
14. {trans-Butene-2 / n-Butane / Ethyl Acetylene
15. cis-Butene-2
16. Unidentified
17. Acetonitrile
18. Acrolein
19. Dimethyl Acetylene
20. Acetone
21. Isopropyl Alcohol
22. {Acrylonitrile / Ethyl Formate
23. Unidentified
24. Unidentified
25. Isoprene
26. Unidentified

was controlled by a preset timer (Dual-Trol), such that the interval between puffs was 60 seconds and the duration of the puff 2 seconds. Lighting the cigarette constituted the first puff. A fresh Cambridge filter was used for each cigarette to separate the particulate phase from the vapor phase.

For colorimetric analysis, reagent solution was injected into a dismantled collection flask (D, Figure 1) with a syringe. The flask stopcocks were then closed, and the flask inserted into a wet ice-bath and connected to the smoking machine manifold at A (Figure 1). At the end of the fourth puff, the sample flask was opened to the manifold at A and evacuated. After 45 seconds, the stopcock (B) on the vacuum line was closed, and after 60 seconds, a puff of smoke was automatically pulled into the flask (D) during the 2-second interval. The flask was then closed, removed, and its contents thoroughly shaken prior to colorimetric analysis.

For gas chromatographic analysis, aliquots of the smoke gas were extracted from the manifold by means of sampling valves, and admitted immediately into the carrier gas stream of the chromatographic column. The volume of gas admitted to the column was regulated by the length of loops (C, Figure 1) on the sampling valves.

Analytical Methods: Table 1 lists the vapor phase constituents determined and the various methods used in the present study.

Measurement of Burn Temperature: The burn temperature of each cigarette was measured by means of a Pt/Pt-13% Rh thermocouple, 2 mil., threaded through a needle hole placed 15 mm from the burning end of the cigarette. Calibrated voltage changes were recorded on a Sargent strip-chart recorder with a 12.5 mV range plug. (See Table 2 for average burn temperatures.)

RESULTS AND DISCUSSION

Anaytical techniques: Two general modes of analysis, colorimetry and gas chromatography, were used to first determine levels of vapor phase constituents in smoke from commercial and reference cigarettes, and subsequently to monitor changes in the vapor phase of cigarette smoke from treated (i.e. with additive) cigarettes. The final data thus obtained, and presented in Table 2, represent averages of 10 or more values for concentration levels of each constituent determined. For example, the raw data for levels of hydrogen sulfide, determined colorimetrically (8), and acrolein, methanol, acetaldehyde, acetonitrile and acetone, determined gas chromatographically, in the smoke generated on the fifth puff from a series of control cigarettes are presented in Tables 3 and 4, respectively, and illustrate the spread of values generally obtained.

Data, presented in Tables 2 and 4, for acrolein, acetonitrile, acetaldehyde, acetone and methanol were obtained from a gas chromatogram similar to the one shown in Figure 2. Although many vapor phase constituents were well separated under the conditions used (Table 1), the methanol, unfortunately, was eluted with the methyl chloride and the methyl acetylene. From preliminary data obtained at conditions other than those used during this study, it was determined that in general methanol was the main contributor to the peak shown in the chromatogram.

To further evaluate the reliability of our methods, we compared our results for levels of vapor phase constituents from commercial cigarettes with the results of other investigators. As can be seen in Table 5, the results are comparable.

Effects of additives: Additives screened in this investigation include some examined previously by Miller *et al.* (4) as possible burn-temperature modifiers, and others such as sodium nitrate which has been of interest to other workers (5) and azo-bis-isobutyronitrile (VAZO), a free radical initiator. While a number of these additives produced some effect on the burn temperature of cigarettes (Table 2) and the burn rate (Table 6), no correlation could be established between a change in burn temperature and a change in the composition of the vapor phase of smoke. However, some significant changes in the composition of the smoke gas were observed, and must be attributed to the presence of the additives in the tobacco. The pertinent data are summarized in Table 2. As can be seen, the most noticeable effects were shown with the addition of sodium nitrate and nickel oxalate to cigarettes. Effects of each of the additives are discussed below, relative to the reference cigarettes.

1. *Sodium nitrate*—The reported effects (5) of sodium nitrate in reducing the tumorigenicity and the concentration levels of a number of components (i.e., nicotine, benzo(a)pyrene, particulate matter) of cigarette smoke led us to investigate the effects of this additive on the vapor phase of smoke, as well; the vapor phase is known to contain compounds which display ciliostatic and other activity (6). Our findings have appeared (12), and are presented here again, but revised (Table 2) to show even greater difference when the data are compared

Table 1. Analytical Methods By Colorimetry	
Constituent Determined	Method
Hydrogen sulfide	Jacobs (8)
Formaldehyde	Jacobs (8)
Hydrogen cyanide	Murty and Viswanathan (9)
Nitrogen Oxides	Saltzman (10)
Sulfur dioxide	West and Ordoveza (11)
	By g.l.p.c.[a]
Hydrogen / Oxygen / Methane / Carbon monoxide	10 ft. x 0.25 in. o.d. column of 40-60 mesh molecular sieve 13X; flow rate 125 ml/min; ambient column temperature; thermal conductivity detection
Carbon Dioxide / Nitrous oxide / Ethane / Ethylene	10 ft. x 0.25 in. o.d. column of 80-100 mesh Polypak II; flow rate 46 ml/min; ambient column temperature; thermal conductivity detection
Acrolein / Acetonitrile / Acetaldehyde / Acetone / Methanol[b]	10 ft. x 0.125 in. o.d. column of Polypak II; flow rate 45 ml/min; column temperature programmed from 50°-170° C at 3.5°/min and from 170°-225°C at 2.8°/min; hydrogen flame detection (see Figure 2).

[a] *Determinations were based on measurements of peak heights; peaks were characterized by retention time comparisons and co-chromatography with standard mixtures of known compounds.*
[b] *Includes methyl chloride and methyl acetylene.*

Table 2. Summary of analyses of vapor phase constituents in the smoke from modified cigarettes (85mm—non-filter)

Component	No Additive (Reference)	8.3% Sodium Nitrate	10% Basic Mag. Carbonate	10% Catalyst $MoO_3 + Al_2O_3$	10% Lead Borate Glass	10% Nickel Oxalate	8% Benzothiazyl Disulfide	10% Hz-1 Catalyst	10% Vazo*
						MOL %			
H_2	0.82	1.64	1.42	1.05	0.65	2.19	0.08	0.85	0.68
O_2	14.01	12.46	12.82	16.26	15.12	10.21	17.14	14.24	15.08
CO	1.78	3.55	2.88	2.49	1.36	4.13	0.34	1.90	1.42
CO_2	5.46	7.86	6.97	5.74	4.91	8.84	1.96	5.18	4.64
						Mcq/35 ML Puff			
NO, NO_2	15.2	48.7	23.8	22.0	22.8	24.7	4.4	20.3	12.1
N_2O	<1.0	11.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
HCN	13.2	23.3	22.4	12.8	18.7	23.4	4.7	16.5	22.3
H_2S	1.5	0.3	3.2	3.1	0.2	2.6	3.5	1.7	2.7
SO_2	1.9	2.7	2.6	2.4	1.8	3.1	2.8	2.6	3.3
Methane	69.9	90.0	119.9	90.0	57.4	124.9	7.5	79.9	59.9
Ethane	22.9	36.4	36.5	26.6	19.5	43.9	3.3	26.5	21.4
Ethylene	10.7	21.5	18.8	14.3	10.1	23.8	1.7	11.8	8.7
Acetaldehyde	46.9	146.3	68.5	51.0	37.4	66.4	3.9	40.3	30.2
Acetone	27.0	55.3	33.7	23.4	21.9	35.9	3.3	22.8	35.2
Acetonitrile	12.8	29.0	13.4	11.4	10.0	13.3	1.7	9.1	9.1
Acrolein	5.7	18.4	9.6	8.2	5.5	10.7	0.5	5.8	4.5
Formaldehyde	4.9	5.6	2.4	5.5	5.6	7.1	3.4	5.2	3.4
Methanol									
Methyl Chloride } Methyl Acetylene }	24.1	55.2	36.0	22.5	17.1	33.4	1.4	17.2	13.5
Avg. Burn Temp.-°C	821	788	804	829	802	771	849	824	828

*AZO-bis-isobutyronitrile

with that from unmodified cigarettes prepared in similar manner. The results indicate that sodium nitrate has the effect of increasing the concentration levels of a number of vapor phase constituents (i.e. nitrogen oxides, acetaldehyde, acrolein) that might better be reduced in, if not removed entirely from, cigarette smoke.

2. *Basic magnesium carbonate ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$)*—Cigarettes containing 10% (by weight) of basic magnesium carbonate burned in an erratic manner. Compared to the reference cigarette, the concentration of most of the vapor phase constituents (i.e. hydrogen cyanide, carbon monoxide, aldehydes, hydrocarbons, hydrogen sulfide and sulfur dioxide) increased significantly.

3. *Reforming catalyst (MoO_3 and Al_2O_3)*—The composition of the smoke gas from cigarettes containing 10% (by weight) of petroleum reforming catalyst (MoO_3 on alumina gel) remained essentially unchanged from that of the reference cigarette.

4. *Lead borate glass*—Lead oxide and boron oxide in the proportions of 81 to 19 respectively were fused to form a homogeneous glass, which after reduction to 200 mesh, was mixed with tobacco (10% "glass" to 90% tobacco). Cigarettes containing this tobacco-additive mix produced a smoke gas which, with the exception of nitric oxide and hydrogen cyanide, contained slightly lower levels of the measured components than were found in the vapor phase of the reference cigarettes. The concentration level of hydrogen sulfide was reduced considerably (from 1.5 in the reference to 0.2 μg in the treated cigarette). The effects observed with lead borate glass may have been due, in part, to the packing properties of the additive and the resulting dilution of the mainstream smoke with air more readily drawn through the cigarette.

5. *Nickel Oxalate*—Cigarettes fabricated with 10%, by weight, of nickel oxalate gave a measurable depression ($\Delta 50°C$) in the burn temperature. A considerably greater level of combustion products was observed in the smoke gas, with a corresponding decrease in the quantity of oxygen. The level of most of the vapor phase constituents was increased by a factor of 2. Even though the burn temperature was lower than that of the reference cigarette, the degree of combustion was apparently greater.

6. *Benzothiazyl disulfide*—Cigarettes modified with benzothiazyl disulfide (10%) were difficult to light, and burned very slowly. The additive tended to form a gummy mass with the tobacco in the burning cone of the ciga-

Table 3. H_2S in cigarette smoke gases (85mm control cigarette).

Method: Colorimetric

Run No.	Burn Temp. °C	Mcg/35 ml puff
1	826	3.6
2	856	5.2
3	824	5.4
4	840	4.9
5	814	4.2
6	844	4.9
7	851	4.0
8	835	3.8
9	817	3.1
10	843	5.5
11	797	4.5
12	854	5.5
13	822	5.5
14	830	4.0
Average	832	4.5
S.D.		0.8
% S.D.		17.8

Table 4. Acrolein, methanol, acetaldehyde, acetonitrile and acetone in cigarette smoke gases (85mm control)

Method: G.C.—Polypak II—Flame Detection

Run No.	Burn Temp. °C	Acrolein	Methanol[a]	Acetaldehyde	Acetonitrile	Acetone
1	842	7.4	28.1	60.5	12.8	35.0
2	837	12.1	50.6	98.0	18.0	49.0
3	857	8.1	35.1	72.7	14.3	41.3
4	821	10.7	33.0	68.3	13.4	37.9
5	855	9.4	35.7	76.5	16.0	46.1
6	816	6.0	23.2	43.6	11.1	27.3
7	855	9.2	37.2	68.1	13.4	40.1
8	846	9.8	37.1	76.5	14.6	43.2
9	835	8.9	36.3	74.0	13.5	38.4
10	863	8.2	35.6	69.9	13.6	36.5
11	807	8.2	35.6	70.7	12.9	38.2
12	847	11.4	43.3	101.1	17.9	50.9
13	832	10.3	39.1	82.6	15.0	43.8
Average	839	9.2	36.1	74.0	14.3	40.6
S.D.		1.7	6.6	14.7	2.0	6.2
% S.D.		18.5	18.3	19.9	14.0	15.3

[a] May include methyl chloride and methyl acetylene.

rette. The small quantities of combustion products found were due probably to dilution of the mainstream smoke with air which was drawn around, rather than through, the burning cone of the tobacco. There were relatively high levels of oxygen, hydrogen sulfide and sulfur dioxide, but the latter two originated, most likely, from the additive.

Miller, Freeman and Stedman had found, previously, that benzothiazyl disulfide was a promising temperature elevator in cigarettes (4).

7. *HZ-1 Catalyst*—Houdry Laboratories catalyst, HZ-1, had the effect of slightly increasing the levels of hydrocarbons, nitric oxide, hydrogen cyanide and sulfur dioxide, and decreasing, to a small extent, levels of acetaldehyde, acetone and acetonitrile in the smoke gas.

8. *Vazo (Azo-bis-isobutyronitrile)*—Lower levels of some of the combustion products, especially carbon

Table 5. Composition of the vapor phase from burning cigarettes.

	This investigation Commercial (non-filter 85 mm- 35 ml puff)	Laboratory fabricated	Newsome et al. (7) (non-filter 40 ml puff)	Osborne et al. (13) (non-filter 35 ml puff)
	mol %			
H_2	1.38	0.82	—	—
O_2	13.46	14.01	—	—
CO	3.00	1.78	—	3.3
CO_2	7.43	5.46	—	8.0
	Mcg/puff			
NO, NO_2	22.9	15.2	30	—
N_2O	<1.0	<1.0	—	—
HCN	23.0	13.2	32	45
H_2S	4.5	1.5	3.4	—
SO_2	3.0	1.9	—	—
Methane	107.5	69.9	97	150
Ethane	37.8	22.9	51	46
Ethylene	17.0	10.7	22	22
Acetaldehyde	74.0	46.9	81	76
Acetone	40.6	27.0	42	48
Acetonitrile	14.3	12.8	—	—
Acrolein	9.2	5.7	8.2	—
Methanol	} 36.1	} 24.1	13	23
Methyl Chloride			19	79
Methyl Acetylene			0.7	—
Formaldehyde	5.3	4.9	4.1	—

Table 6. Burn Rates for Control and Modified Cigarettes (to 30mm Butt Length).

	Total Burn Time, Minutes*
Commercial Cigarette (Control)	8.22
Lab Fabricated Cigarette (Reference)	11.04
8.3% Sodium Nitrate	10.34
10% Magnesium Carbonate	9.43
10% Reforming Catalyst (MoO_3)	10.39
10% Nickel Oxalate	9.31
10% Lead Borate Glass	9.37
8% Benzothiazyl Disulfide	18.03
10% Cracking Catalyst (HZ-1)	9.43
10% VAZO (Azo-bis-isobutyronitrile)	10.49

Average of 2 or more determinations

monoxide and carbon dioxide, were found in the cigarette smoke gas with "VAZO", a free-radical initiator, added to the cigarette tobacco. Hydrogen cyanide, acetone, hydrogen sulfide and sulfur dioxide, however, were substantially increased in the smoke gas with this additive.

CONCLUSIONS

The data presented herein show that certain additives, particularly those which supply oxygen to the combustion process, influence, to some extent, the composition of cigarette smoke gas. Sodium nitrate, nickel oxalate and basic magnesium carbonate were most effective in changing this composition. In general, these additives lowered combustion temperatures and raised concentration levels of combustion products. Burn rates were altered, to some extent, by modifications to the tobacco, and the corresponding change in number of puffs must be considered when evaluating the total quantity of a combustion product delivered to the smoker. While cigarettes modified with sodium nitrate are known to produce lower levels of tumor inducing constituents (in the particulate phase), similar information for the other additives, which were investigated during this study, is lacking.

In general, none of the additives tested dramatically effected the removal of smoke components (in the vapor phase) regarded as detrimental to health, while some even produced adverse effects. In a few instances, favorable effects, such as the marked reduction of concentration levels of hydrogen sulfide with sodium nitrate and

with lead borate glass were noted.

During the course of this investigation, it was noted that vapor phase composition is a function not only of tobacco and/or additive intermixed with it, but also of the packing and orientation of the tobacco (or additive) within the cigarette, the porosity of the cigarette paper, and the length of the cigarette. In fact, by physically modifying the cigarette, one might more easily effect greater (and more significant) changes in the level of components in the smoke gas than by the use of additives. In a subsequent paper, the relationship between physical design of the cigarette and the composition of the vapor phase will be discussed.

SUMMARY

A number of additives, in modified cigarettes, were tested for their effects on the composition of the vapor phase of cigarette smoke. Based on this study, further work with other selected additives is indicated. Although many of the additives effected some compositional changes, no outstanding reductions of those vapor phase components alleged to be detrimental to health were observed.

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